

On the Quantum Theory of Vibration-Rotation Bands. By J. R. OPPENHEIMER. (Communicated by Mr R. H. FOWLER.)

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1. The frequencies of the lines in the vibration-rotation spectrum of a diatomic molecule may be obtained unambiguously by the application of the classical quantum dynamics to a simple molecular model. The dominant term in the intensities of these lines has been obtained by Fowler* from the summation rules; this, and the next term, were computed by Kemble† from an application of the correspondence principle to a three-dimensional model. But the details of these calculations are not free from ambiguity. For, in the first case, the weight of the states, and, in the second, the method of averaging over transitions, is arbitrary. For the outer lines of the band this ambiguity is negligible; for the inner ones, and particularly for the missing central line, it is not.

Now the new mechanics ‡ gives a precise solution of this problem, and might accordingly be expected to decide definitely the intensity of the null line, and the value of the higher terms in the intensities of the outer lines. The purpose of this note is to obtain the solution, and to compare it with previous results, and with the results of experiment.

The problem has been treated by Brillouin§. Brillouin's chief conclusions are (1) that, contrary to the contention of Heisenberg||, the new mechanics does not necessarily give the same energies as the classical theory with the introduction of half-integral quantum numbers; and (2) that, if Heisenberg's result were correct, the new mechanics would account for the disappearance of the central line. He uses Cartesian coordinates $(q_1 q_2)$, and their corresponding momenta $(p_1 p_2)$. He imposes the constraint

$$q_1^2 + q_2^2 = a^2,$$

and the single quantum condition

$$(1) \quad [q_1 p_1] + [q_2 p_2] = i$$

for the rotational motion, where $[ab]$ is the Poisson Bracket of

* Fowler, *Phil. Mag.* vol. XLIX, p. 1272 (1925).

† Kemble, *Phys. Rev.* vol. XXV, p. 1 (1925).

‡ Dirac, *Proc. Roy. Soc. A*, vol. CX, p. 561 (1926); Born, Heisenberg, Jordan, *Zeit. f. Physik*, vol. XXXV, p. 557 (1926).

§ Brillouin, *C.R.* vol. CLXXXII, p. 374 (1926).

|| Heisenberg, *Zeit. f. Physik*, vol. XXX, p. 879 (1925); Born und Jordan, *Zeit. f. Physik*, vol. XXXIV, p. 858 (1925).

a and *b*. On the other hand, the Heisenberg-Dirac* quantum conditions reduce, in this case, to a single condition

$$\left[(q_1 p_2 - q_2 p_1), \frac{q_1 + iq_2}{(q_1^2 + q_2^2)^{\frac{1}{2}}} \right] = i \frac{q_1 + iq_2}{(q_1^2 + q_2^2)^{\frac{1}{2}}}$$

which cannot be reduced to the form (1). Moreover, in the Hamiltonian used by Brillouin the coupling of the kinetic energies of rotation and vibration is neglected. Finally, the problem is treated in two dimensions, so that we should not expect † correct values for the intensities. Brillouin does not give his solution in detail. He does give the intensities for the case of vanishing coupling, and for this case gets the same intensities for all lines of a band. But it may readily be shown that the differential equation is regular, uniformly in the coupling parameter λ as this tends to zero. It follows that the argument cannot explain the absence of the central line for the small finite values of λ which occur. In fact we shall show that, in the two-dimensional case, the central line would be present.

2. *The dynamical problem.* We may take for model two point-atoms attracting each other radially. If the masses of the atoms be m_1 and m_2 , then the classical Hamiltonian, after the elimination of the centre of gravity, becomes

$$(2) \quad H = \frac{1}{2\mu} (p_x^2 + p_y^2 + p_z^2) + U_1(x^2 + y^2 + z^2),$$

where

$$(3) \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}; \quad x = x_1 - x_2;$$

$$(m_1 + m_2) p_x = m_2 p_{x_1} - m_1 p_{x_2}.$$

Since we shall not ultimately want $x_1 y_1 z_1, x_2 y_2 z_2$, and since the elimination of the centre of gravity (3) holds in the quantum theory, we may take (2) as Hamiltonian. There is as yet no adequate reason for not choosing some classically equivalent form. The only other result which we shall take over directly from the classical theory is the expression for the energy radiated per second. We shall use this in terms of Cartesian coordinates and accelerations ‡; and we shall not be inconsistent if we take the Hamiltonian in terms of them.

In the classical solution it is convenient to use polar angle variables. These cannot be represented by matrices, and we shall

* Dirac, *Proc. Roy. Soc. A*, vol. cx, p. 561 (1926).

† Kemble, *Phys. Rev.* vol. xxv, p. 1 (1925).

‡ Heisenberg, *Zeit. f. Physik*, vol. xxxiii, p. 879 (1925); Born und Jordan, *Zeit. f. Physik*, vol. xxxiv, p. 858 (1925).

accordingly adopt the more general methods developed by Dirac*. We want a canonical transformation to uniformizing variables such that xyz shall be periodic in the angle variables. Classically we should obtain this by three successive transformations: introduction of polar coordinates, in which the Hamilton-Jacobi equation separates; elimination of the nodes; and uniformization of the vibration-rotation. Dirac† has shown that there is a canonical transformation equivalent to the first two:

$$(4) \quad r^2 = x^2 + y^2 + z^2; \quad p_r = \frac{x}{r} p_x + \frac{y}{r} p_y + \frac{z}{r} p_z - \frac{i\hbar_*}{r},$$

$$\epsilon^{i\mathfrak{S}} = r^{-1} k^{\frac{1}{2}} (k_2^2 - p^2)^{-\frac{1}{2}} (z + i [kz]) k^{\frac{1}{2}};$$

$$k^2 = \frac{1}{2} \hbar_*^2 + \Sigma_x m_x^2 = \frac{1}{2} \hbar_*^2 + \Sigma_x (y p_x - z p_y)^2,$$

$$\epsilon^{i\phi} = (k^2 - p_2^2)^{-\frac{1}{2}} (m_x + i m_y); \quad p = x p_y - y p_x,$$

where $p_2 = p - \frac{1}{2} \hbar_*$, $k_2 = k - \frac{1}{2} \hbar_*$, $\hbar_* = \frac{1}{2\pi} \hbar$.

[In general we write $\alpha_1 = \alpha + \frac{1}{2} \hbar_*$; $\alpha_2 = \alpha - \frac{1}{2} \hbar_*$, if α is an action variable.] We shall use only the following information about this transformation:

1. It is canonical.
2. The values of xyz obtained by the inversion of (4) are:

$$(5) \quad z = \frac{1}{2} r (\omega_2 \epsilon^{i\mathfrak{S}} + \omega_1 \epsilon^{-i\mathfrak{S}}),$$

$$\left. \begin{matrix} x \\ iy \end{matrix} \right\} = \frac{r}{4i} [\omega_{22} \epsilon^{i\mathfrak{S} + i\phi} \pm \omega_{21} \epsilon^{i\mathfrak{S} - i\phi} - \omega_{12} \epsilon^{-i\mathfrak{S} + i\phi} \pm \omega_{11} \epsilon^{-i\mathfrak{S} - i\phi}],$$

where $\omega_1^2 = 1 - \frac{p_1 p_2}{k(k + \hbar_*)}$; $\omega_2^2 = 1 - \frac{p_1 p_2}{k(k - \hbar_*)}$;

$$\omega_{11}^2 = \frac{(k + p_1)(k + p_1 + \hbar_*)}{k(k + \hbar_*)}.$$

$$(6) \quad \omega_{12}^2 = \frac{(k - p_2)(k - p_2 + \hbar_*)}{k(k + \hbar_*)}; \quad \omega_{21}^2 = \frac{(k - p_1)(k - p_1 - \hbar_*)}{k(k - \hbar_*)};$$

$$\omega_{22}^2 = \frac{(k + p_2)(k + p_2 - \hbar_*)}{k(k - \hbar_*)}.$$

3. The transformed Hamiltonian is

$$(7) \quad H = \frac{1}{2\mu} \left(p_r^2 + \frac{k_1 k_2}{r^2} \right) + U(r).$$

The third transformation requires certain hypotheses about U ; in analogy with the classical solution‡ we shall suppose that the

* Dirac, *Proc. Roy. Soc. A*, vol. cx, p. 561 (1926); Born, Heisenberg, Jordan, *Zeit. f. Physik*, vol. xxxv, p. 557 (1926).

† Dirac, *Proc. Roy. Soc. A*, vol. cxI, p. 281 (1926).

‡ Born, *Atommechanik*, § 20.

molecule can rotate uniformly; that this rotation is stable; and that the amplitude of the oscillations about it which do in fact occur is small compared with the mean distance of separation of the atoms. Then we must have

$$\dot{p}_r = [p_r H] = 0; \quad \dot{r} = [r H] = 0; \quad k_1 k_2 = \mu r^3 [U'(r), p_r]$$

when we substitute the proper quantum numbers for k , and the corresponding c -number for r . We shall take over this c -formula, which may be justified physically, and write

$$(8) \quad \frac{k_1 k_2}{\mu a^3(k)} = [U p_r]_{r=a(k)} = U'(a) \text{ (Def.)},$$

where k and a are q -numbers. Further, we set $r = a(k) + \rho$, and thus obtain from (1) and (8), the expansion

$$(7a) \quad H = \frac{k_1 k_2}{2\mu a^2(k)} + \frac{1}{2\mu} (p_r^2 + \omega^2 \rho^2) + \lambda \rho^3 - \dots$$

which converges by hypothesis. In (7a)

$$\omega^2 = \mu U''(a) + \frac{3k_1 k_2}{a^4(k)} = \omega_0^2 + \frac{3k_1 k_2}{a^4(k)}; \quad \lambda = \frac{1}{6} U'''(a) - 4 \frac{k_1 k_2}{2\mu a^5}.$$

We may note further that

$$[\rho p_r] = 1, \quad [\rho k] = 0,$$

but that

$$(9) \quad [\rho \mathfrak{D}] = -[\mathfrak{D}] = \frac{2k}{\omega^2 a^3(k)}.$$

The retention of first order terms in λ does not affect the frequencies, but changes the intensities. It follows, however, from the form of the transformation for r and \mathfrak{D} , that the relative intensities of lines in the same band will be changed only by a factor of the order of $k^2 J^{\frac{1}{2}} / a^5 \omega^{\frac{1}{2}}$, which is small compared with the terms we shall retain, and too small for experimental detection. The new mechanics is, of course, applicable to the more general case; but the transformation, even in the simplest case, where $U'''(a) \sim 0$, is very cumbersome. We shall accordingly neglect λ and observe that our results will not give us the intensities in the overtone bands.

The transformation

$$(10) \quad r = \frac{1}{i(2\omega)^{\frac{1}{2}}} (J^{\frac{1}{2}} \epsilon^{i\omega} - \epsilon^{-i\omega} J^{\frac{1}{2}}) + a; \quad p_r = \left\{ \frac{1}{2}\omega \right\}^{\frac{1}{2}} (J^{\frac{1}{2}} \epsilon^{i\omega} + \epsilon^{-i\omega} J^{\frac{1}{2}}),$$

$$k = k, \quad \mathfrak{D} = \tau + \alpha;$$

$$\alpha = - \left(\frac{2}{\omega} \right)^{\frac{1}{2}} \cdot \frac{k}{a^2 \omega} (J^{\frac{1}{2}} \epsilon^{i\omega} + \epsilon^{-i\omega} J^{\frac{1}{2}}) - \frac{3k}{4a^4 \omega^2 i}$$

$$\times \{ J^{\frac{1}{2}} (J - h)^{\frac{1}{2}} \epsilon^{2i\omega} - \epsilon^{-2i\omega} J^{\frac{1}{2}} (J - h)^{\frac{1}{2}} \},$$

$$p = p, \quad \phi = \phi$$

defines the new canonical variables (J, ω) , (k, τ) , (p, ϕ) . If we assume that these satisfy the quantum conditions, we get at once

$$[kp] = [kp_r] = [pp_r] = [\phi p_r] = [\phi \mathfrak{D}] = [\phi k] = [\phi \gamma] = 0;$$

$$[p\phi] = [k\mathfrak{D}] = -1.$$

Moreover

$$(11) \quad [rp_r] = -[p_r r] = \frac{1}{i\hbar_*} \frac{1}{2i} (2J - 2\epsilon^{-i\omega} J \epsilon^{i\omega}) = 1,$$

$$(12) \quad i(\rho p_r + p_r \rho) = (J - \hbar)^{\dagger} J^{\dagger} \epsilon^{2i\omega} - \epsilon^{-2i\omega} J^{\dagger} (J - \hbar)^{\dagger}$$

and

$$(13) \quad p_r^2 + \omega^2 \rho^2 = \frac{1}{2} \omega (2J + 2\epsilon^{-i\omega} J \epsilon^{i\omega}) = 2\omega J_1.$$

From the first of these (11) it follows that r and p_r are canonical.

From the second (12) we get, neglecting powers of $\frac{k\sqrt{\mu}}{a^2\omega}$ above the second,

$$[\mathfrak{D}r] = -\frac{3k\mu\rho}{2a^4\omega^2} + \frac{3k\mu}{4a^4\omega^2} [p_r \rho + \rho p_r, \rho] - \frac{2k}{a^2\omega^2} + \frac{2}{\omega} \frac{k}{a^2\omega} [rp_r] = 0,$$

$$\text{and} \quad [\mathfrak{D}p_r] = +\frac{3k\mu p_r}{2a^4\omega^2} - \frac{3k\mu}{4a^4\omega^2} [p_r \rho + \rho p_r, p_r] = 0.$$

Assuming therefore that the new variables satisfy the quantum conditions, we have shown that the old variables satisfy all the quantum conditions. This establishes the transformation. The asymmetry of r and p_r , and thus of W , in J , is not peculiar to this problem. It has its analogue in the harmonic oscillator, for which

$$|q(n, n+1)|^2 \propto n+1.$$

3. *Frequencies, Quantum Numbers.* By (7 a) and (13)

$$(14) \quad W = W(Jk) = \frac{k_1 k_2}{2\mu a^2(k)} + \frac{\omega J_1}{\mu}.$$

This differs from the classical value in having J_1 for J , and $k_1 k_2$ for k^2 .

Before we can find the frequencies, we must decide how to assign the quantum numbers, n, m, s , corresponding to the action variables J, k, p . The hypothesis of a normal state for the vibratory motion means that n must be integral. The argument by which m and s are determined is strictly analogous to that given by Dirac* and Born, Heisenberg, and Jordan† for the Zeeman effect of an atom with one series electron. We should expect s to be so chosen that

$$\left| \frac{p_1 p_2}{k(k - \hbar_*)} \right| \leq 1; \quad \left| \frac{p_1 p_2}{k(k + \hbar_*)} \right| \leq 1,$$

since, otherwise by (5) z might not be real for reals s and m . This means

* Dirac, *Proc. Roy. Soc. A*, vol. cxi, p. 281 (1926).

† Dirac, *Proc. Roy. Soc. A*, vol. cx, p. 561 (1926); Born, Heisenberg, Jordan, *Zeit. f. Physik*, vol. xxxv, p. 557 (1926).

that s may vary from $-m + \frac{1}{2}$ to $+m - \frac{1}{2}$; it is readily seen from the values we get for the intensities (18), that all transitions from s values within this range to those outside are forbidden. Finally, we may choose m to give a normal state for which a transition with decreasing m is impossible. In this case the only physical justification for such an assumption is the observed absence of the central line*. We shall show that the central line does not vanish if the only condition on m is Brillouin's condition of symmetry for positive and negative rotations.

With this assignment of quantum numbers (clearly s is irrelevant) we get for the absorption frequencies

$$(14 a) \quad \nu(n, m \rightarrow n+1, m \pm 1) = \frac{h}{8\pi^2\mu a^2(0)} \left(\mp 2m + 1 - \frac{h^2(m \pm \frac{1}{2})^3}{\pi^2 a^4(0)\omega_0^2} \dots \right) \\ + \nu_1(n + \frac{3}{2}) - \nu_2(n + \frac{1}{2}), \\ \nu_1 = \frac{\omega(m \pm 1)}{2\pi\mu} \sim \frac{\omega_0}{2\pi\mu} \left(1 + \frac{3\mu h^2(m \pm 1 + \frac{1}{2})(m \pm 1 - \frac{1}{2})}{2a^4(0)\omega_0^2} \right); \\ \nu_2 \sim \frac{\omega_0}{2\pi\mu} \left(1 + \frac{3\mu m_1 m_2 h^2}{2a^4(0)\omega_0^2} \right).$$

The difference between these and the classical frequencies is too small for experimental detection, more particularly since $a(0)$ and ω_0 can only be found from the band itself. The energy differences would, however, give an appreciable term in the specific heats.

4. *Intensities.* We may now compute the *a priori* intensities of the band lines directly. For this we need x, y, z in terms of the final variables. In each case we have several alternative forms. Thus

$$(15) \quad z = \frac{r}{2} (\omega_2 \epsilon^{i\alpha} + \epsilon^{-i\alpha} \omega_2) = \frac{1}{2} (\epsilon^{i\alpha} \omega_1 + \epsilon^{-i\alpha} \omega_2) r = \frac{r}{2} (\omega_2 \epsilon^{i\alpha} + \omega_1 \epsilon^{-i\alpha}) \dots$$

But since all the transformations are canonical, these forms ought to give the same intensities; and it may be readily verified that they do. Now to the second order in $\frac{h}{a^2\omega_0}$, we get, using the expansion for the exponential

$$(16) \quad \epsilon^{i\tau+i\alpha} = \sum_0^\infty \frac{1}{n!} (i\alpha + i\tau)^n \sim \sum_0^\infty \frac{(i\tau)^n}{n!} + \sum_0^{n-1} \frac{(i\tau)^r (i\alpha) (i\tau)^{n-1-r}}{n!} \\ = \sum_0^\infty \frac{n(i\alpha) (i\tau)^{n-1}}{n!} + \sum_0^\infty \frac{(i\tau)^n}{n!} - \sum_0^\infty \frac{n(n-1) i h_* (i\tau)^{n-2} \alpha}{2kn!} \\ = \sum_0^\infty \left(1 + \frac{i\alpha \cdot k_2}{k_2} \right) \frac{(i\tau)^n}{n!} = \left(1 + \frac{i\alpha k_2}{k} \right) \epsilon^{i\tau} = (1 + i\alpha_2) \epsilon^{i\tau}, \\ \epsilon^{-i\tau-i\alpha} = \left(1 - \frac{i\alpha \cdot k_1}{k} \right) \epsilon^{-i\tau} = (1 - i\alpha_1) \epsilon^{-i\tau}.$$

* On Schrödinger's Theory there is no normal state for a rigid rotator in two dimensions, and the transitions for $m, (\frac{1}{2} \rightarrow -\frac{1}{2}), (-\frac{1}{2} \rightarrow \frac{1}{2})$ occur.

Then from (5), (10) and (16),

$$(17) \quad z = \frac{1}{2} \left[a(k) + \frac{1}{i(2\omega)^{\frac{1}{2}}} (J^{\dagger} \epsilon^{i\omega} - \epsilon^{-i\omega} J^{\dagger}) \right] \times \\ \left[\varpi_2 (1 + i\alpha_2) \epsilon^{i\tau} + \varpi_1 (1 - i\alpha_1) \epsilon^{-i\tau} \right], \\ \left. \begin{aligned} x \\ iy \end{aligned} \right\} = \frac{1}{4i} \left[a(k) + \frac{1}{i(2\omega)^{\frac{1}{2}}} (J^{\dagger} \epsilon^{i\omega} - \epsilon^{-i\omega} J^{\dagger}) \right] [\varpi_{22} (1 + i\alpha_2) \epsilon^{i\tau+i\phi} \\ \pm \varpi_{21} (1 + i\alpha_2) \epsilon^{i\tau-i\phi} - \varpi_{12} (1 - i\alpha_1) \epsilon^{-i\tau+i\phi} \mp \varpi_{11} (1 - i\alpha_1) \epsilon^{-i\tau-i\phi}].$$

Now expand $\omega^{-\frac{1}{2}}$ to second order in $\frac{k}{a^2\omega}$, take α_1 and α_2 in front of the exponentials in w , and collect the coefficients of $\epsilon^{i\omega}$ and $\epsilon^{-i\omega}$. This gives for the Zeeman components

(18)

$$\begin{aligned} |z(-1, -1, 0)| &= \frac{1}{2} \left(\frac{n}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_2 [1 - 2\gamma m_2 \{1 + \frac{3}{8}\gamma(m_2 - n)\}], \\ |z(-1, +1, 0)| &= \frac{1}{2} \left(\frac{n}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_1 [1 + 2\gamma m_1 \{1 - \frac{3}{8}\gamma(m_1 + n)\}], \\ |z(+1, -1, 0)| &= \frac{1}{2} \left(\frac{n+1}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_2 [1 + 2\gamma m_2 \{1 - \frac{3}{8}\gamma(m_2 + n + 1)\}], \\ |z(+1, +1, 0)| &= \frac{1}{2} \left(\frac{n+1}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_1 [1 - 2\gamma m_1 \{1 + \frac{3}{8}\gamma(m_1 - n - 1)\}], \\ |x(-1, -1, -1)| &= \frac{1}{4} \left(\frac{n h_*}{2\omega_0} \right)^{\frac{1}{2}} \varpi_{22} [1 - 2\gamma m_2 \{1 + \frac{3}{8}\gamma(m_2 - n)\}], \\ |x(-1, -1, +1)| &= \frac{1}{4} \left(\frac{n h_*}{2\omega_0} \right)^{\frac{1}{2}} \varpi_{21} [1 - 2\gamma m_2 \{1 + \frac{3}{8}\gamma(m_2 - n)\}], \\ |x(-1, +1, -1)| &= \frac{1}{4} \left(\frac{n h_*}{2\omega_0} \right)^{\frac{1}{2}} \varpi_{12} [1 + 2\gamma m_1 \{1 - \frac{3}{8}\gamma(m_1 + n)\}], \\ |x(-1, +1, +1)| &= \frac{1}{4} \left(\frac{n h_*}{2\omega_0} \right)^{\frac{1}{2}} \varpi_{11} [1 + 2\gamma m_1 \{1 - \frac{3}{8}\gamma(m_1 + n)\}], \\ |x(+1, -1, -1)| &= \frac{1}{4} \left(\frac{n+1}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_{22} [1 + 2\gamma m_2 \{1 - \frac{3}{8}\gamma(m_2 + n + 1)\}], \\ |x(+1, -1, +1)| &= \frac{1}{4} \left(\frac{n+1}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_{21} [1 + 2\gamma m_2 \{1 - \frac{3}{8}\gamma(m_2 + n + 1)\}], \\ |x(+1, +1, -1)| &= \frac{1}{4} \left(\frac{n+1}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_{12} [1 - 2\gamma m_1 \{1 + \frac{3}{8}\gamma(m_1 - n - 1)\}], \\ |x(+1, +1, +1)| &= \frac{1}{4} \left(\frac{n+1}{2\omega_0} h_* \right)^{\frac{1}{2}} \varpi_{11} [1 - 2\gamma m_1 \{1 + \frac{3}{8}\gamma(m_1 - n - 1)\}], \\ |y(ijk)| &= |x(ijk)|; \quad |x(ijk)| = |x[(n, m, s) \rightarrow (n+i, m+j, s+k)]|, \end{aligned}$$

where
$$\gamma = \frac{\hbar}{2\pi\omega_0 a^2(0)} = \frac{\hbar}{4\pi^2 \mu a_0^2 \nu_0} = \frac{\nu_r}{\nu_0}.$$

Actually the system is degenerate. Summing the "intensities"

$$I_0(0, m \rightarrow 1, m+1) = \text{const.} [1 - 4\gamma m_1 (1 - \frac{5}{8}\gamma m_1 - \frac{3}{8}\gamma)] \bar{S},$$

$$\begin{aligned} \bar{S} &= \sum_{-m+\frac{1}{2}}^{+m-\frac{1}{2}} \omega_1^2 + \frac{1}{2} \sum_{-m+\frac{1}{2}}^{+m-\frac{1}{2}} (s) \omega_{11}^2 + \frac{1}{2} \sum_{-m+\frac{1}{2}}^{+m-\frac{1}{2}} (s) \omega_{12}^2 \\ &= \frac{1}{2} \sum_{-m+\frac{1}{2}}^{+m-\frac{1}{2}} (\omega_{11}^2 + 2\omega_1^2 + \omega_{12}^2) \\ &= \frac{1}{2} \cdot m \cdot \left(4 + \frac{2}{m}\right) = 4(m + \frac{1}{2}) = 4m_1. \end{aligned}$$

Similarly

$$I_0(0, m+1 \rightarrow 1, m) = 4 \cdot \text{const.} [1 + 4\gamma m_1 (1 + \frac{5}{8}\gamma m_1 - \frac{3}{8}\gamma)] \cdot m_1.$$

The intensity of the central line vanishes. But it would not have vanished if we had made m integral, nor if we had treated the problem in two dimensions.

For the intensities of the \bar{n} th lines* (in energy, and not in quanta)

$$I_+(\bar{n}) \propto \bar{n} (1 - 4\gamma \bar{n} (1 - \frac{5}{8}\gamma \bar{n} - \frac{3}{8}\gamma)) \epsilon^{-\frac{1}{kT}W(0, \bar{n}-\frac{1}{2})} \cdot \nu(0, \bar{n} - \frac{1}{2} \rightarrow 1, \bar{n} + \frac{1}{2}),$$

$$I_-(\bar{n}) \propto \bar{n} (1 + 4\gamma \bar{n} (1 + \frac{5}{8}\gamma \bar{n} - \frac{3}{8}\gamma)) \epsilon^{-\frac{1}{kT}W(0, \bar{n}+\frac{1}{2})} \cdot \nu(0, \bar{n} + \frac{1}{2} \rightarrow 1, \bar{n} - \frac{1}{2}),$$

or, at least for not too large m ,

$$I_+(\bar{n}) \propto \bar{n} \epsilon^{-\frac{1}{kT}W(0, \bar{n})} (1 - 3\gamma \bar{n}) \left(1 + \frac{\bar{n}h^2}{2\mu\alpha_0^2 k\tau}\right),$$

$$I_-(\bar{n}) \propto \bar{n} \epsilon^{-\frac{1}{kT}W(0, \bar{n})} (1 + 3\gamma \bar{n}) \left(1 - \frac{\bar{n}h^2}{2\mu\alpha_0^2 k\tau}\right).$$

This in part† resolves the paradox noted by Fowler. For the two branches are nearly equal in intensity in spite of the assymetry of the temperature factor. The main part of the assymmetric factor which compensates this had been previously obtained by Kemble from the Coriolis forces.

This means that the summation rules do not apply exactly, because the frequency differences of the lines of the band are not negligible. Neglecting the factors $(1 \pm 4\gamma \bar{n} \dots)$ and $\epsilon^{-\frac{1}{kT}W}$, they hold exactly. For the weights of the states are proportional to m .

I should like to thank Mr R. H. Fowler, F.R.S., and Mr P. A. M. Dirac for their criticism and advice.

* Kemble, *loc. cit.* and Fowler, *Phil. Mag.* vol. L, p. 1079 (1925).

† For the fundamental hydrogen chloride band studied by Kemble and Fowler the values of 4γ and $h^2/2\mu\alpha_0^2 k\tau$ differ by only about 10 per cent.; the positive branch remains slightly the stronger.

5. *Summary.* The dynamical problem of the "diatomic molecule" is solved on the new mechanics. The terms of the rotational energy are $A(m^2 - \frac{1}{4})$, where $m = \pm \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$; the weights of the corresponding states are $2m$; the frequencies differ a little from the classical ones. Finally the intensities are slightly different from those computed by Kemble; the main term agrees with that of Fowler, but the positive branch is only slightly stronger than the negative. The central line vanishes. The intensities are valid only for the fundamental band.

6. *Addendum.* This problem has been treated by Schrödinger* by his method of characteristics. Schrödinger does not find the intensities; but he obtains energy terms which give frequencies in agreement with (14) and (14 a). More recently the problem has been treated by Mensing† by the method of matrices in a paper which came to hand just as the writing of this paper was completed. Mensing neglects γ but retains λ . The main terms in the intensities of the fundamental band are, of course, the Zeeman factors of (18). By an application of Born and Jordan's solution for the anharmonic oscillator‡ Mensing also obtains expressions for the intensities in the overtones. It is, however, readily seen from (17) that the terms arising from γ are of the same order as those arising from λ , and that, with the actual values of these constants for the hydrogen halides, the former terms predominate for the outer lines of the overtone bands. It is probably therefore not justified to neglect them and retain λ .

* Schrödinger, *Ann. d. Phys.* vol. LXXIX, p. 484 (1926). See particularly Eq. (51).

† Mensing, *Zeit. f. Physik*, vol. XXXVI, p. 814 (1926).

‡ Born und Jordan, *Zeit. f. Physik*, vol. XXXIV, p. 858 (1925).
